



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS 1963-A

DTIC FILE COPY

12

AD-A185 570

OFFICE OF NAVAL RESEARCH

Contract N00014-84-G-0201

Task No. 0051-865

Technical Report #14

P H T H A L O C Y A N I N E S

By

A.B.P. Lever

in

Chem Tech

DTIC
ELECTE
OCT 15 1987
S D

York University
Department of Chemistry
4700 Keele St., North York
Ontario, Canada M3J 1P3

Reproduction in whole, or in part, is permitted for any purpose of the United States Government

*This document has been approved for public release and sale; its distribution is unlimited

*This statement should also appear in Item 10 of the Document Control Data-DD form 1473. Copies of the form available from cognizant contract administrator

87 10 6 14

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY Unclassified		3. DISTRIBUTION/AVAILABILITY OF REPORT As it appears on the report	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE		4. PERFORMING ORGANIZATION REPORT NUMBER(S) Report # 14	
4. PERFORMING ORGANIZATION REPORT NUMBER(S)		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
6a. NAME OF PERFORMING ORGANIZATION A.B.P. Lever, York University Chemistry Department	6b. OFFICE SYMBOL (if applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research	
6c. ADDRESS (City, State, and ZIP Code) 4700 Keele St., North York, Ontario M3J 1P3 Canada		7b. ADDRESS (City, State, and ZIP Code) Chemistry Division 800 N. Quincy Street Arlington, VA 22217 U.S.A.	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-84-G-0201	
8c. ADDRESS (City, State, and ZIP Code)		10. SOURCE OF FUNDING NUMBERS	
		PROGRAM ELEMENT NO.	PROJECT NO.
		TASK NO.	WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) Phthalocyanines			
12. PERSONAL AUTHOR(S) Lever, A.B.P.			
13a. TYPE OF REPORT Technical	13b. TIME COVERED FROM Aug/86 TO Aug/87	14. DATE OF REPORT (Year, Month, Day) December 1986	15. PAGE COUNT 16
16. SUPPLEMENTARY NOTATION			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	
		phthalocyanine, review of uses	
19. ABSTRACT (Continue on reverse if necessary and identify by block number)			
<p>A review of the myriad of uses to which phthalocyanines are put, or may potentially be put in the future. <i>Handwritten note: This is a review of the electrocatalytic properties of phthalocyanine molecules in organic synthesis, biology and medicine, and a list of references is included.</i></p>			
20. DISTRIBUTION AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Unclassified/unlimited	
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. Robert K. Grasselli		22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Attn: Code 1113 800 N. Quincy Street Arlington, Virginia 22217-5000	2	Dr. David Young Code 334 NORDA NSTL, Mississippi 39529	1
Dr. Bernard Douda Naval Weapons Support Center Code 50C Crane, Indiana 47522-5050	1	Naval Weapons Center Attn: Dr. Ron Atkins Chemistry Division China Lake, California 93555	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko, Code L52 Port Hueneme, California 93401	1	Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12 high quality	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
DTNSRDC Attn: Dr. H. Singerman Applied Chemistry Division Annapolis, Maryland 21401	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
Dr. William Tolles Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000	1	Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1



Accession For	
NTIS CRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution _____	
Approved _____	
Date _____	
A-1	

ABSTRACTS DISTRIBUTION LIST, 359/627

- Dr. Manfred Breiter
Institut für Technische Elektrochemie
Technischen Universität Wien
9 Getreidemarkt, 1160 Wien
AUSTRIA
- Dr. E. Yeager
Department of Chemistry
Case Western Reserve University
Cleveland, Ohio 44106
- Dr. R. Sutula
The Electrochemistry Branch
Naval Surface Weapons Center
Silver Spring, Maryland 20910
- Dr. R. A. Marcus
Department of Chemistry
California Institute of Technology
Pasadena, California 91125
- Dr. J. J. Auborn
AT&T Bell Laboratories
600 Mountain Avenue
Murray Hill, New Jersey 07974
- Dr. M. S. Wrighton
Chemistry Department
Massachusetts Institute
of Technology
Cambridge, Massachusetts 02139
- Dr. B. Stanley Pons
Department of Chemistry
University of Utah
Salt Lake City, Utah 84112
- Dr. Bernard Spielvogel
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709
- Dr. Mel Miles
Code 3852
Naval Weapons Center
China Lake, California 93555
- Dr. P. P. Schmidt
Department of Chemistry
Oakland University
Rochester, Michigan 48063
- Dr. Roger Belt
Litton Industries Inc.
Airtron Division
Morris Plains, NJ 07950
- Dr. Ulrich Stimming
Department of Chemical Engineering
Columbia University
New York, NY 10027
- Dr. Royce W. Murray
Department of Chemistry
University of North Carolina
Chapel Hill, North Carolina 27514
- Dr. Michael J. Weaver
Department of Chemistry
Purdue University
West Lafayette, Indiana 47907
- Dr. R. David Rauh
EIC Laboratories, Inc.
Norwood, Massachusetts 02062
- Dr. Edward M. Eyring
Department of Chemistry
University of Utah
Salt Lake City, UT 84112
- Dr. M. M. Nicholson
Electronics Research Center
Rockwell International
3370 Miraloma Avenue
Anaheim, California
- Dr. Nathan Lewis
Department of Chemistry
Stanford University
Stanford, California 94305
- Dr. Hector D. Abruna
Department of Chemistry
Cornell University
Ithaca, New York 14853
- Dr. A. B. P. Lever
Chemistry Department
York University
Downsview, Ontario M3J 1P3

ABSTRACTS DISTRIBUTION LIST, 359/627

Dr. Martin Fleischmann
Department of Chemistry
University of Southampton
Southampton SO9 5H UNITED KINGDOM

Dr. John Wilkes
Department of the Air Force
United States Air Force Academy
Colorado Springs, Colorado 80840-6528

Dr. R. A. Osteryoung
Department of Chemistry
State University of New York
Buffalo, New York 14214

Dr. Janet Osteryoung
Department of Chemistry
State University of New York
Buffalo, New York 14214

Dr. A. J. Bard
Department of Chemistry
University of Texas
Austin, Texas 78712

Dr. Steven Greenbaum
Department of Physics and Astronomy
Hunter College
695 Park Avenue
New York, New York 10021

Dr. Donald Sandstrom
Boeing Aerospace Co.
P.O. Box 3999
Seattle, Washington 98124

Mr. James R. Moden
Naval Underwater Systems Center
Code 3632
Newport, Rhode Island 02840

Dr. D. Rolison
Naval Research Laboratory
Code 6171
Washington, D.C. 20375-5000

Dr. D. F. Shriver
Department of Chemistry
Northwestern University
Evanston, Illinois 60201

Dr. Alan Bewick
Department of Chemistry
The University of Southampton
Southampton, SO9 5NH UNITED KINGDOM

Dr. Edward Fletcher
Department of Mechanical Engineering
University of Minnesota
Minneapolis, Minnesota 55455

Dr. Bruce Dunn
Department of Engineering &
Applied Science
University of California
Los Angeles, California 90024

Dr. Elton Cairns
Energy & Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Dr. Richard Pollard
Department of Chemical Engineering
University of Houston
Houston, Texas 77004

Dr. M. Philpott
IBM Research Division
Mail Stop K 33/801
San Jose, California 95130-6099

Dr. Martha Greenblatt
Department of Chemistry, P.O. Box 939
Rutgers University
Piscataway, New Jersey 08855-0939

Dr. Anthony Sammells
Eltron Research Inc.
4260 Westbrook Drive, Suite 111
Aurora, Illinois 60505

Dr. C. A. Angell
Department of Chemistry
Purdue University
West Lafayette, Indiana 47907

Dr. Thomas Davis
Polymers Division
National Bureau of Standards
Gaithersburg, Maryland 20899

ABSTRACTS DISTRIBUTION LIST, 359/627

Dr. Stanislaw Szpak
Naval Ocean Systems Center
Code 633, Bayside
San Diego, California 95152

Dr. Gregory Farrington
Department of Materials Science
and Engineering
University of Pennsylvania
Philadelphia, Pennsylvania 19104

Dr. John Fontanella
Department of Physics
U.S. Naval Academy
Annapolis, Maryland 21402-5062

Dr. Micha Tomkiewicz
Department of Physics
Brooklyn College
Brooklyn, New York 11210

Dr. Lesser Blum
Department of Physics
University of Puerto Rico
Rio Piedras, Puerto Rico 00931

Dr. Joseph Gordon, II
IBM Corporation
5600 Cottle Road
San Jose, California 95193

Dr. Joel Harris
Department of Chemistry
University of Utah
Salt Lake City, Utah 84112

Dr. J. O. Thomas
University of Uppsala
Institute of Chemistry
Box 531 Baltimore, Maryland 21218
S-751 21 Uppsala, Sweden

Dr. John Owen
Department of Chemistry and
Applied Chemistry
University of Salford
Salford M5 4WT UNITED KINGDOM

Dr. O. Stafsudd
Department of Electrical Engineering
University of California
Los Angeles, California 90024

Dr. Boone Owens
Department of Chemical Engineering
and Materials Science
University of Minnesota
Minneapolis, Minnesota 55455

Dr. Johann A. Joebstl
USA Mobility Equipment R&D Command
DRDME-EC
Fort Belvoir, Virginia 22060

Dr. Albert R. Landgrebe
U.S. Department of Energy
M.S. 6B025 Forrestal Building
Washington, D.C. 20595

Dr. J. J. Brophy
Department of Physics
University of Utah
Salt Lake City, Utah 84112

Dr. Charles Martin
Department of Chemistry
Texas A&M University
College Station, Texas 77843

Dr. Milos Novotny
Department of Chemistry
Indiana University
Bloomington, Indiana 47405

Dr. Mark A. McHugh
Department of Chemical Engineering
The Johns Hopkins University
Baltimore, Maryland 21218

Dr. D. E. Irish
Department of Chemistry
University of Waterloo
Waterloo, Ontario, Canada
N2L 3G1

DL/1113/87/2

ABSTRACTS DISTRIBUTION LIST, 359/627

Dr. Henry S. White
Department of Chemical Engineering
and Materials Science
151 Amundson Hall
421 Washington Avenue, S.E.
Minneapolis, Minnesota 55455

Dr. Daniel A. Buttry
Department of Chemistry
University of Wyoming
Laramie, Wyoming 82071

Dr. W. R. Fawcett
Department of Chemistry
University of California
Davis, California 95616

Dr. Peter M. Blonsky
Eveready Battery Company, Inc.
25225 Detroit Road, P.O. Box 45035
Westlake, Ohio 44145

ABSTRACTS DISTRIBUTION LIST, 051A

DL/1113/87/2

Dr. M. A. El-Sayed
Department of Chemistry
University of California
Los Angeles, California 90024

Dr. E. R. Bernstein
Department of Chemistry
Colorado State University
Fort Collins, Colorado 80521

Dr. J. R. MacDonald
Chemistry Division
Naval Research Laboratory
Code 6110
Washington, D.C. 20375-5000

Dr. G. B. Schuster
Chemistry Department
University of Illinois
Urbana, Illinois 61801

Dr. J. B. Halpern
Department of Chemistry
Howard University
Washington, D.C. 20059

Dr. M. S. Wrighton
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Dr. W. E. Moerner
I.B.M. Corporation
Almaden Research Center
650 Harry Rd.
San Jose, California 95120-6099

Dr. A. B. P. Lever
Department of Chemistry
York University
Downsview, Ontario
CANADA M3J1P3

Dr. George E. Walrafen
Department of Chemistry
Howard University
Washington, D.C. 20059

Jr. Joe Brandelik
AFWAL/AADO-1
Wright Patterson AFB
Fairborn, Ohio 45433

Dr. Carmen Ortiz
Consejo Superior de
Investigaciones Cientificas
Serrano 121
Madrid 6, SPAIN

Dr. Kent R. Wilson
Chemistry Department
University of California
La Jolla, California 92093

Dr. G. A. Crosby
Chemistry Department
Washington State University
Pullman, Washington 99164

Dr. Theodore Pavlopoulos
NOSC
Code 521
San Diego, California 91232

Dr. John Cooper
Code 6173
Naval Research Laboratory
Washington, D.C. 20375-5000

Dr. Joseph H. Boyer
Department of Chemistry
University of New Orleans
New Orleans, Louisiana 70148

Dr. Harry D. Gafney
Department of Chemistry
Queens College of CUNY
Flushing, New York 11367-0904

P H T H A L O C Y A N I N E S

By A.B.P.Lever Dept. of Chemistry, York University,
North York, Ontario Canada M3J 2P3

Introduction

In 1928, at Grangemouth, Scotland, traces of a blue material were found at the works of Messrs. Scottish Dyes Ltd., during the preparation of phthalimide from phthalic anhydride. This intense blue material was later demonstrated to be ferrous phthalocyanine. Thus was born an industry initially based upon dyes but now rapidly developing into many other fields.

Phthalocyanines (Pc) (Fig.1) are generally blue or green in their normal oxidation state, intensely coloured in the solid, usually with a characteristic purple sheen when crystalline. Numerous X-ray structures have generally, though not exclusively, shown a square planar arrangement of the Pc unit about the central metal atom. Virtually every metallic element, and a few non-metallic elements, form phthalocyanines. The formation of square planar species provides two axial sites at which additional chemistry frequently occurs. In a sense, the phthalocyanines form a Periodic Table of their own in which each MPc has a chemistry dictated by the element and its Pc environment. This therefore provides for a wealth of different applications for these species, tuned by the central ion, by the axial ligation, by substituents in the phthalocyanine ring, and by the phthalocyanine environment [1,2]. There are currently

some 4900 different phthalocyanines known, and some 6000 references discussing them since 1967.

In addition to their extensive use as green and blue colorants for a wide range of paints, textiles, plastics, and metal surfaces, the intense colour of these materials lends itself especially to the production of inks. Most dark blue ink ball point pens are phthalocyanine based.

In the following discussion, we explore some of the uses being developed for phthalocyanines, providing leads to the literature, but certainly not in a comprehensive fashion, given the space available.

Electrocatalysis

Metal phthalocyanines are growing in importance as electrocatalysts. Over a decade ago, their use as oxygen reduction catalysts began to develop as a possible replacement for platinum in fuel cell cathodes. CoPc and FePc are especially effective as oxygen reduction electrocatalysts. Both these species can be dispersed in a carbon electrode to generate water or hydrogen peroxide as oxygen reduction product depending upon factors such as pH [3]. Tetrasulfonated iron and cobalt phthalocyanines reduce oxygen in aqueous phase and have been studied as monolayers on ordinary pyrolytic graphite electrodes as a means of investigating detailed mechanisms [4]. Earlier work showing that poorly defined binuclear and polymeric phthalocyanines were better at oxygen reduction than mononuclear phthalocyanines led to the synthesis of well defined soluble (organic solvent), binuclear phthalocyanines, with neopentoxy sidechains, which are also effective at oxygen reduction [5]. Rather unexpectedly a thin film of PtPc has also been shown to be

effective in oxygen reduction [6]. Cobalt(II) phthalocyanine, and, with less activity nickel phthalocyanine, have recently been shown to electrocatalytically reduce carbon dioxide generating formic acid at pH 2-7 [7].

The oxidation of a range of sulphur systems such as thiols, e.g. cysteine and hydrogen sulphide [8] has been studied, especially in Russia using CoPc [9]. Cobalt and iron tetrasulfonated phthalocyanines (MTsPc) are more effective than Mn, Ni or Cu systems. The electroreduction of cystine has also been studied, with MnTsPc being most effective [10]. The oxidation of sulphur dioxide to sulfuric acid, has also been studied catalytically [11] and electrocatalytically [12,13]. Virtually all the first row transition metal phthalocyanines are active with Mn, Fe and CoPc being the most active [12]. Some interesting spectroscopic studies of the reaction of OVPc with hydrogen sulphide have also been reported [14]. Sulphur compound oxidation catalysis has potential use in the clean-up of sulfur-containing effluents. Many other substrates have been oxidised catalytically or electrocatalytically by metallophthalocyanines; among these are included hydrogen peroxide [15] and hydrazine [16].

Photovoltaics

Thin-film phthalocyanines on electrodes have potential industrial importance as photovoltaic devices, and in the design of display devices (vide infra) [17]. Thin film sandwich photovoltaic cells composed of a transparent metal electrode, commonly gold, and a thin film of a metal phthalocyanine (e.g. ClAlPc, FAlPc, ClGaPc, ClInPc, VOPc, TlOPc, H2Pc), and a blocking contact, commonly aluminum, have proven to be relatively

efficient (2-10%, photocurrent quantum efficiency) [18,19]. The use of an aluminum phthalocyanine with surfactant substituents (on the aluminum) also seems promising [20]. Other sandwich electrodes which have been studied include a thin film of n-type CdS laid upon In/SnO₂, with a p-type MPc on the CdS followed by a gold film. Mg and ZnPc are effective in this mode, but, again ClAlPc and ClInPc appear more efficient [21]. Photo-electrochemical cells of the type metal oxide semi-conductor electrode/-sensitizer/redox electrolyte/Pt electrode have been fabricated using metallophthalocyanines as the sensitizer. Here the intent can be the photovoltaic generation of energy with no net change in redox electrolyte, or photo-production of chemical products therein (e.g. water oxidation). Most of the first row transition metal MPcs have been tested in this fashion [22a]. The photoelectric behaviour of Langmuir-Blodgett films of copper phthalocyanine, have also been studied [22b].

Photocatalysis

In related studies, MPc systems have been screened as photocatalysts for water reduction to hydrogen [23]. In multi-component sacrificial systems, many main group and transition metal MPcs can photocatalytically reduce methyl viologen, providing a pathway to molecular hydrogen. These molecules are likely to be more chemically stable than analogous porphyrins but the quantum yields are generally very small.

Molecular Metals

Metal phthalocyanines tend to form crystals in which phthalocyanine molecules pack parallel to one another. If these are 'partially' oxidised, the charge propagates along the chain generating a so-called unidimensional conductor. For example iodine oxidation of CoPc and NiPc lead to CoPcI and NiPcI which contain, formally, $(MPc)_3^+ I_3^-$ units stacked in a regular fashion. In the former case the oxidation is associated with the cobalt atoms and leads to conductivity comparable with Pt-Pt stacked systems, while in the latter case, oxidation occurs at the ring providing rather different behaviour. Despite the difference in electronic structure, the crystal structures are almost identical [24]. Iodine doped FAlPc and FGaPc also look very promising in this context [25]. Iodine doping is not the only procedure for making these species. Compounds such as $NiPc(BF_4)_{0.33}$ also have high conductivities [26]. These 'molecular metals' may prove to have industrially useful properties.

Photoconductivity

There has been immense interest in the photoconductive properties of metallophthalocyanines. Phthalocyanines, such as X-PcH₂ (a polymorph of metal-free phthalocyanine prepared by grinding to a very finely divided state) have photoconductive properties which make them especially useful for photocopying devices. Many commercial photocopiers use phthalocyanine derivatives as the active light sensitive medium, though information on these species is generally buried in the patent literature.

Electrochromism

Lanthanides and actinides form di-phthalocyanine complexes of general formula MPC_2 . The metal ion is sandwiched between two roughly parallel phthalocyanine units being 8-coordinated by the central nitrogen atoms. Of especial interest is the electrochromic behaviour of many of these species, investigated in particular by Kirin and by Nicholson. Lutetium diphthalocyanine, for example, exists in a range of oxidation states having violet, blue and green and yellow-red colours. Polarisation of an electrode assembly containing $LuPc_2$ generates a color depending upon the potential applied [27]. Mono-phthalocyanine systems seem less suitable for this purpose, though a recent study of octacyano-phthalocyanines showed electrochromic behaviour for metal-free, zinc and copper species [28]. Other di-phthalocyanines such as $SnPc_2$ may also be useful. The use of Langmuir-Blodgett films [29] shows promise with metal-free phthalocyanine having been shown to be electrochromic therein [30]. Electrochromic phthalocyanines are being intensely investigated as display devices of considerable industrial promise.

Chemical Sensors

When a phthalocyanine is placed on, or between, electrode surfaces, some property of this device may 'respond' to the presence of incoming molecules permitting the design of a sensor which may detect such molecules at ppm to ppb levels. In this respect, the semi-conductor properties of the phthalocyanines can be utilised. If a Langmuir-Blodgett film of MPC is placed on a planar micro-electrode array, a current is obtained when the device is biased. When the film is sensitive to other

chemical molecules, a change in current may be used to monitor their concentration [31]. Such a device is called a chemiresistor [32]. Using an interdigitated microelectrode array and a tetracumylphenoxy substituted CuPc, it is possible to detect ammonia vapour below 0.5ppm, by monitoring current flow. The device is also sensitive to other donor molecules such as NO₂ (1ppm), but not to non-donor molecules such as benzene [32]. Various patents have been awarded for the development of gas sensors (frequently oxygen) which involve MPcs. For example, this is accomplished using a metal-air electrochemical cell, in contact with air, having an anode impregnated with various polymeric MPcs, including Fe, Mn, Co, Ni, Cu, Mo, and also non-polymeric PbPc [33], Fe, Pt and PdPc [34].

A moderately selective sensor for NO₂ (1ppb - 10ppm) is obtained by exposing a PbPc (or H₂Pc) film, at temperatures above 100°C, to NO₂ and monitoring the change in electrical conductivity [35]. A modification of this technology is the use of a phthalocyanine modified electrode (CoPc/carbon paste) as a detector of hydrazine in chromatography [36].

Batteries

There is considerable interest in the development of high energy density batteries. Primary and secondary lithium battery systems are under intense development, and both may use phthalocyanines as electrocatalysts. They involve a carbon cathode impregnated with electrocatalyst, and a lithium metal anode. Primary cells (non-rechargeable) use thionyl chloride as 'solvent' and redox active species. The thionyl chloride is reduced at the cathode, with phthalocyanine electrocatalysts, inter alia, being used to increase the discharge rate of such cells.

FePc and CoPc are seen to be effective, but CuPc is much less so. Polymeric $(\text{FePc})_n$ and $(\text{CoPc})_n$ species apparently have greater stability [37]. Phthalocyanine catalysed sulfuryl chloride cells are also under investigation [38].

Secondary lithium cells (rechargeable) use propylene carbonate as solvent. Phthalocyanines have proven to be effective catalysts in improving the discharge voltage characteristics of such cells. FePc, CuPc, CoPc, MnPc, AlClPc, ClGaPc, Cl₂SnPc and metal-free phthalocyanines are among those found to be active. Copper octacyanophthalocyanine and copper poly-phthalocyanine also appear to be useful [39,40]. Secondary cells may also be constructed using metal phthalocyanine polymerically bound to the anode, with zinc as the cathode, and the electrolyte facilitating the $\text{I}_2 \rightarrow 2\text{I}^-$ redox reaction, e.g. Fe(III), Co(II), and Cu(II) tetracarboxyphthalocyanines bound to poly(2-vinylpyridine-co-styrene) [41].

Biological and Medical Opportunities

Phthalocyaninines are being investigated in the area of photo-toxicity. Thus one might impregnate a cancerous tumour with a phthalocyanine and shine light, perhaps via a laser passed through a fibre optic, onto the site. The phthalocyanine is excited and causes destruction of the tumour. This possibility has great promise as a means of destroying cancerous tumours [42]. Nerves may be 'stained' with a phthalocyanine, and then the nerve energised. Monitoring of the physical properties of the phthalocyanine in such circumstances provides a non-destructive method of probing nerve behaviour [43]. At a more mundane level, staining sutures blue makes them easier to observe inside the

operation site [44]. These various possibilities all rely upon the very low toxicity of MPC systems under normal ground state conditions. Various workers have studied the replacement of heme by metallophthalocyanines in protein environments [45].

Miscellaneous

Finally note that substitution of a suitable long chain into metal-free phthalocyanine generates a liquid crystalline material [46], several MPC systems can be induced to lase [47,48] and can be used as phototropic filters for laser applications [48], and electroluminescent diodes can be constructed from phthalocyanine Langmuir-Blodgett films [49]. 'Photochemical hole burning' involves laser irradiation of metal free phthalocyanine at a specific frequency within an inhomogenously broadened absorption line. The result is a persistent reduction in absorption intensity. Such a phenomenon can be used to store information. Thus, via this procedure, phthalocyanines may have value for high density reviews of other uses and features of phthalocyanines, the reader is dire

In this article we have briefly touched upon the considerable interest being shown in phthalocyanines. We confidently expect that this interest will grow and diversify and that phthalocyanines will have a major role to play in industry in the future.

Bibliography

- 1 A.B.P.Lever, *Adv.Inorg.Chem.Radiochem.*, 7 (1965) 27; A.B.P.Lever, S.Licoccia, K.Magnell, P.C.Minor and B.S.Ramaswamy, *ACS Sym.Ser.*, 201 (1981) 4015.
- 2 a) F.H.Moser and A.H.Thomas, 'The Phthalocyanines', CRC Press, Boca Raton, 1983, vols.I,II; b) D.Wohrle, *Adv.Polym.Sci.*, 50(1983) 45.
- 3 F.Beck, W.Dammert, J.Heiss, H.Hiller and R.Polster, *Z.Naturforsch.*, 28A (1973) 1009; T.Hirai, J.Yamaki and A.Yamaji, *J.Appl.Electrochem.*, 15 (1985) 77. F.Van den Brink, W.Visscher and E.Barendrecht, *J.Electroanal.Chem.*, 175 (1984) 279; 172 (1984) 301; 157 (1983) 283,305; C.A.Melendres and X.Feng, *J.Electroanal.Chem.*, 130 (1983) 811; A.J.Appleby, M.Savy and P.Caro, *J.Electroanal.Chem.*, 111 (1980) 91; S.Maroie, M.Savy and J.J.Verbist, *Inorg.Chem.*, 18 (1979) 2560; T.Hirai and J.Yamaki, *J.Electrochem.Soc.*, 132 (1985) 2125; T.Osaka, K.Naoi, T.Hirabayashi and S.Nakamura, *Bull.Chem.Soc.Jpn.*, 59(1986) 2717.
- 4 S.Zececic, B.Simic-Glavaski, E.Yeager, A.B.P.Lever and P.C.Minor, *J.Electroanal.Chem.*, 196 (1985) 339.
- 5 C.C.Leznoff, S.Greenberg, S.M.Marcuccio, P.C.Minor, P.Seymour and A.B.P.Lever, *Inorg.Chim.Acta*, 89 (1984) L35; S.M.Marcuccio, P.I.Svirskaya, S.Greenberg, A.B.P.Lever, C.C.Leznoff and K.B.Tomer, *Can.J.Chem.*, 63 (1985) 623, 3057.
- 6 C.Paliteiro, A.Hamnett and J.B.Goodenough, *J.Electroanal.Chem.*, 160 (1984) 359.
- 7 C.M.Lieber and N.S.Lewis, *J.Am.Chem.Soc.*, 106 (1985) 5033; S.Kapusta and N.Hackerman, *J.Electrochem.Soc.*, 131 (1984) 1511.
- 8 W.M.Brouwer, P.Piet and A.L.German, *Makr.Chem.*, 185 (1984) 363.
- 9 Chemical Abstracts CA 103:144165a, 122764t, 42312d, 39483e.

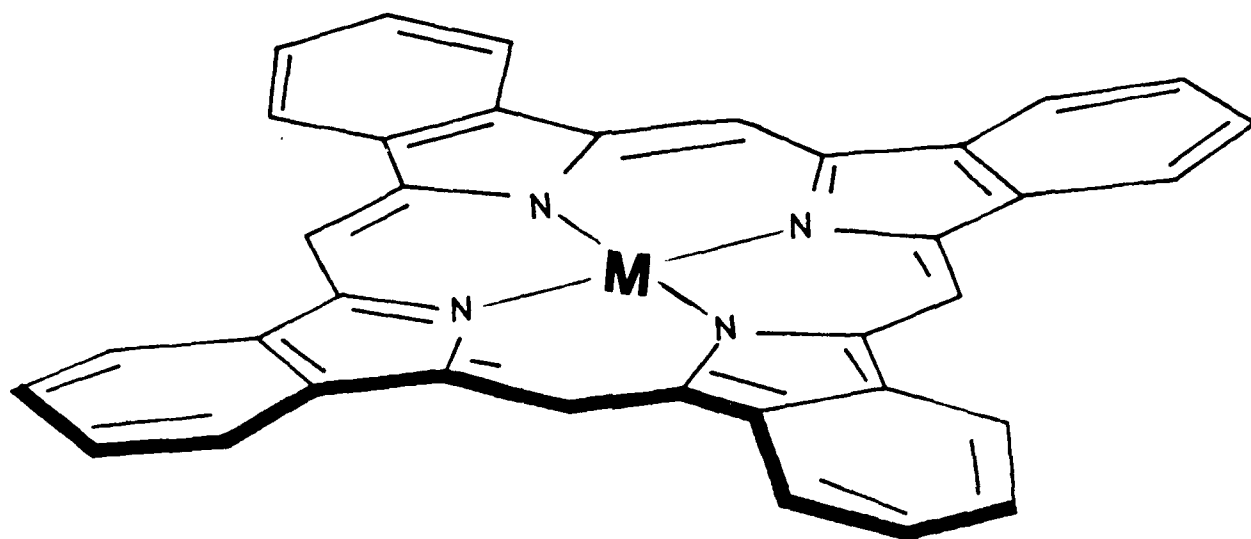
- 102:203467e. 101:75194d. 10 0:177465q, 92011p, 92010n. 99:72965k.
- 10 J.H.Zagal, and P.Herrera, *Electrochim.Acta*, 30 (1985) 449.
- 11 S.D.Boyce, M.R.Hoffman, A.P.Hong and L.M.Moberley, *Environ.Sci.Tech.*, 17 (1983) 602 and *Chemical Abstracts CA* 100:196934
- 12 M.R.Tarasevich and E.A.Akhundov, *Zh.Prikl.Khim.* (Leningrad) 56 (1983) 316. (see *Chemical Abstracts CA* 98:169149q).
- 13 K.A.Radyushkina, M.R.Tarasevich and E.A.Akhundov, *Elektrokhimiya*, 14 (1978) 810.
- 14 P.C.H.Mitchell and J.A.Valero. *Inorg.Chim.Acta* 71 (1983) 179.
- 15 G.I.Zakharkin and M.P.Tarasevich, *Elektrokhimiya*, 11 (1975) 1019.
- 16 J.Zagal and S.Ureta-Zanartu, *J.Electroanal.Chem.*, 129 (1982) 2242; J.H.Zagal, *J.Electroanal.Chem.*, 109 (1980) 389.
- 17 M.J.Green and L.R.Faulkner, *J.Am.Chem.Soc.*, 105 (1983) 2950; V.I.Gavrilov, N.V.Butusova, E.A.Luk'yanets and I.V.Shelepin, *Elektrokhimiya*, 16 (1980) 1611; J.Nakata and I.Takeshi, *Oyo Butsuri*, 54(1985) 65; M.A. Ben Said, S.Belgacem, M.Dachraoui, R.Bennaceur and H.Bouchriha, *Rev.Phys.Appl.*, 21(1986) 407.
- 18 R.O.Loutfy, C.K.Hsiao and R.Ho, *Can.J.Phys.*, 61 (1983) 1416; Le H. Dao and G.Perrier, *Chem.Lett.* (1986) 1259; T.Klofta, W.F.Buttner and N.R.Armstrong, *J.Electrochem.Soc.*, 133(1986) 1531.
- 19 P.C.Riecke and N.R.Armstrong, *J.Phys.Chem.*, 89 (1985) 1121; T.J.Klofta, P.C.Riecke, C.A.Linkous, W.J.Buttner, A.Nanthakumar, T.D.Mewborn and N.R.Armstrong, *J.Electrochem.Soc.*, 132 (1985) 2134; M.Shimura and A.Toyoda, *Jpn.J.Appl.Phys*, part 1, 23 (1984) 1462.
- 20 J.P.Dodelet, H.P.Pommier and M.Ringuet, *J.Appl.Phys.*, 53 (1982) 4270; D.Belanger, J.P.Dodelet, L.H.Dao and B.A.Lombos, *J.Phys.Chem.*, 88(1984) 4288; M.F.Lawrence, J.P.Dodelet and L.H.Dao, *J.Electroanal.Chem.*, 131 (1984) 2977.

- 21 A.M.Hor and R.O.Loutfy, *Can.J.Chem.*, 61 (1983) 901; A-M.Hor, R.O.Loutfy and C-K.Hsiao, *Appl.Phys.Lett.*, 42 (1983) 165.
- 22 a) F-R.Fan and L.R.Faulkner, *J.Am.Chem.Soc.* 101 (1979) 4779; A.Girardeau, F-R.Fan and A.J.Bard, *J.Am.Chem.Soc.*, 102 (1980) 5137; b) M.Yoneyama, M.Sugi, M.Saito, K.Ikegami, S.Kuroda and S.Iizima, *Jpn.Appl.Phys.*, Part 1, 25(1986) 961.
- 23 J.R.Darwent, P.Douglas, A.Harriman, G.Porter and M-C.Richoux, *Coord. Chem.Rev.*, 44 (1982) 83; A.B.P.Lever, S.Licocchia, B.S.Ramaswamy, A.Kandil and D.V.Stynes, *Inorg.Chim.Acta*, 51 (1981) 169.
- 24 J.Martinsen, J.L.Stanton, R.L.Greene, J.Tanaka, B.M.Hoffman and J.A.Ibers, *J.Am.Chem.Soc.*, 107 (1985) 6915; C.J.Schramm, R.P.Scaringe, D.R.Stojakovic, B.M.Hoffman, J.A.Ibers, and T.J.Marks, *J.Am.Chem.Soc.*, 102(1980) 6702; W.J.Pietro, T.J.Marks and H.A.Ratner, *J.Am.Chem.Soc.*, 107 (1985) 5387.
- 25 R.S.Nohr, P.M.Kuznesof, K.J.Wynne, M.E.Kenney and P.G.Siebenman, *J.Am.Chem.Soc.*, 103 (1981) 4371.
- 26 T.Inabe, S.Nakamura, W-B.Liang, T.J.Marks, R.L.Burton, C.R.Kannewurf and K.Imaeda, *J.Am.Chem.Soc.*, 107 (1985) 7224.
- 27 G.C.S.Collins and D.J.Schiffirin, *J.Electroanal.Chem.*, 139 (1982) 335; H.Yamamoto, M.Noguchi and M.Tanaka, *Jpn.J.Appl.Phys.*, 23 (1984) 221; M.M.Nicholson and F.A.Pizzarello, *J.Electroanal.Chem.*, 128 (1981) 1288, 1740; G.A.Corker, B.Grant and N.J.Clecak, *J.Electroanal.Chem.*, 126 (1979) 1339; P.N.Moskalev and I.S.Kirin, *Zh.Fiz.Khim.*, 46 (1972) 778; J.C.Marchon, *J.Electroanal.Chem.*, 129 (1982) 377; M.M.Nicholson, *Ind.Eng.Chem.Prod.Res.Dev.*, 21 (1981) 261; M.M'sadak, J.Roncali and F.Garnier, *J.Electroanal.Chem.*, 189(1985) 99; G.C.S.Collins and D.J.Schiffirin, *J.Electroanal.Chem.*, 132 (1985) 1835.
- 28 B.Schumann, D.Wohrle and N.I.Jaeger, *J.Electroanal.Chem.*, 132 (1985)

- 2144.
- 29 G.J.Kovacs, P.S.Vincett and J.H.Sharp, *Can.J.Phys.*, 63 (1985) 346; A.W.Snow and N.L.Jarvis, *J.Am.Chem.Soc.*, 106 (1984) 4706; S.Baker, M.C.Petty, G.G.Roberts and M.V.Twigg, *Thin Solid films*, 99 (1983) 53.
- 30 H.Yamamoto, T.Sugiyama and M.Tanaka, *Jpn.J.Appl.Phys.* pt.2 24 (1985)305.
- 31 R.L.van Ewyk, A.V.Chadwick and J.D.Wright, *J.Chem.Soc., Far. I*, 76 (1980) 2194; 77 (1981) 73. J.D.Wright, A.V.Chadwick, B.Meadows, J.J.Miasik, *Mol.Cryst.Liq.Cryst.*, 93 (1983) 315.
- 32 H.Wohltjen, W.R.Barger, A.R.Snow and N.L.Jarvis, *IEEE Transactions on electron Devices*, 32 (1985) 1170; S.Baker, G.G.Roberts and M.C.Petty, *IEEE Proc. part I, Solid-state electron devices*, 130 (1983) 260.
- 33 Japan patents 59/138942; 59/138943; 59/26052 1984; 56/94252 1981.
- 34 S.Kuwata, N.Yiura, N.Yamazoe and T.Seiyama, *Nippon Kagaku Kaishi*, 1984 1232.
- 35 B.Bott and T.A.Jones, *Sensors and Actuators*, 5 (1984) 43.
- 36 K.M.Korfhage, K.Ravichandran and R.P.Baldwin, *Anal.Chem.*, 56 (1984) 1514.
- 37 M.Madou, K.Kinoshita, M.C.H.McKubre and S.Szpak, *Proc.Electrochem.Soc.*, 84-12 (1984) 618; N.Doddapaneni, *Proc.Electrochem.Soc.*, 84-12 (1984) 630; H.V.Venkatesetty, US Patent 4,279,973 (1981); N.Doddapaneni, D.L.Chua and J.T.Nelson, *Proc. 30th Power Source Symp.*, 1982, p.169,201; N.Doddapaneni, *Proc.31st Power Source Symp.* (1984) 411.
- 38 N.Doddapaneni, *Proc.Electrochem.Soc.*, 84-1 (Lithium batteries) (1984) 122; German patent 1983 DE 3236042 A1.
- 39 J.Yamaki and A.Jamaji, *J.Electroanal.Chem.*, 129 (1982) 5; D.Wohrle, M.Kirschenbaum and N.I.Jaeger, *J.Electroanal.Chem.*, 132 (1985) 1150.
- 40 M.Arakawa, J.Yamaki and T.Okada, *J.Electroanal.Chem.*, 131 (1984) 2605.

- 41 O.Hirabaru, T.Nakase, K.Hanabusa, K.Shirai, K.Takemoto and N.Hojo, *Polymer Commun.* 25 (1984) 284.
- 42 J.D.Spikes, *Photochem.Photobiol.* 43(1986) 691; N.Brasseur, H.Ali, D.Autenrieth, R.Langlois and J.E. Van Lier, *Photochem.Photobiol.*, 42(1985) 515; E.Ben-Hur and I.Rosenthal, *Photochem.Photobiol.*, 42(1985) 129; Idem *Int.J.Radiat.Biol.Relat.Stud.Phys.,Chem.Med.*, 47(1985) 145; W.S.Chan, R.Svensen, D.Phillips and I.R.Hart, *Br.J.Cancer.* 53(1986) 255.
- 43 B.Simic-Glavaski, *Cell.Biophys.* 7(1985) 205; D.L.Rosental, *Tsitologiya*, 21(1979) 408; L.D.Rosental, S.V.Levin and G.I.Sergeeva, *Tsitologiya*, 19(1977) 361; L.D.Rosental and S.V.Levin, *Tsitologiya*, 18(1976) 1090; K.M.Kirpichnikova, S.V.Levin and D.L.Rosental, *Biofiz.Membr.* (1973) 316.
- 44 a) United States Food and Drug Administration, *Fed.Registry* 50(1985) 16227; b) *Fed.Registry*, 48(1983) 34946.
- 45 D.V.Stynes, S.Liu and H.Marcus, *Inorg.Chem.*, 24(1985) 4335; L.Ostropolska and H.Przywarska-Boniecka, *CA104:170541*; H.Przywarska-Boniecka and L.Ostropolska, *J.Inorg.Biochem.*, 20(1984) 103; L.Trynda, *Inorg.Chim.Acta*, 78(1983) 229; H.Przywarska-Boniecka and L.Ostropolska, *J.Inorg.Biochem.*, 16(1982) 183; J.P.Leicknam, O.E.Anitoff, M.J.H.Gallice, M.Henry and A.E.K.Tayeb, *J.Chim.Phys. Phys-Chim. Biol.*, 78 (1981) 587; H.Przywarska-Boniecka and H.Swirska, *J.Inorg.Biochem.*, 13(1980) 283.
- 46 A.Skoulios, C.Piechocki, J.Simon and P.Weber, *Mol.Cryst.Liq.Cryst.*, 100 (1983) 275.
- 47 R.Kugel, A.Svirnickas, J.J.Katz and J.C.Hindman, *Opt.Commun.*, 23 (1977) 189
- 48 see Ref.2, vol.II, p.65.

- 49 J.Batey, M.C.Petty, G.G.Roberts and D.R.Wright, *Electron.Lett.*, 20 (1984) 489. 50 L.Kador, G.Schulte and D.Haarer, *J.Phys.Chem.*, 90(1986) 1264; W.E.Moerner, *J.Molec.Electronics*, 1(1985)55; H.W.H.Lee, A.L.Huston, M.Gehrtz and W.E.Moerner, *Chem.Phys.Lett.*, 114(1985) 491; M.Romagnoli, W.E.Moerner, F.M.Schellenberg, M.D.Levenson and C.G.Bjorklund, *J.Opt.Soc.Am.B: Opt.Phys.*, 1 (1984) 341; A.Gutierrez, G.Castro, G.Schulte and D.Haarer, *Springer Ser. Solid-state Sci.*, 49(1983) 206; A.R.Gutierrez, *Chem.Phys.Lett.*, 74(1980) 293.



END

DATE

FILMED

DEC.

1987